

8122

(12) **UK Patent Application** (19) **GB** (11) **2 230 022** (13) **A**
(43) Date of A publication 10.10.1990

(21) Application No 9006428.8

(22) Date of filing 22.03.1990

(30) Priority data

(31) 8906607

(32) 22.03.1989

(33) GB

(71) Applicant

BP Chemicals Limited

(Incorporated in the United Kingdom)

**Belgrave House, 76 Buckingham Palace Road,
London, SW1W 0SU, United Kingdom**

(72) Inventor

Peter Stewart Cartwright

(74) Agent and/or Address for Service

S K Krishnan

**BP International Limited, Patents & Agreements
Division, Chertsey Road, Sunbury-on-Thames,
Middlesex, TW16 7LN, United Kingdom**

(51) INT CL⁵

C11D 3/12

(52) UK CL (Edition K)

**C5D DHC D118 D120 D141 D168 D169 D173 D175
D180**

(56) Documents cited

EP 0156187 A1

(58) Field of search

**UK CL (Edition J) C5D
INT CL⁴ C11D**

(54) **Detergent formulations**

(57) This invention relates to detergent powder formulations comprising a surfactant, a builder salt and a clay. The clay is pretreated with material such as a siloxane prior to incorporation in the formulation. The formulations impart softness to the fabrics washed therewith. Alternative pretreatment materials are polyacrylate, dialkyl citrate, alkoxylated dialkyl citrate, bis (alkyl polyoxyalkylene) citrate, alkoxylated N-alkyl alkanolamide, alkoxylated glycerol mono-and di-stearates, and betaines.

GB 2 230 022 A

DETERGENT FORMULATIONS

The present invention relates to detergent formulations containing clay as a component. Most detergent formulations have primarily performed the function of cleansing the fabrics washed whereas the softening of the washed fabric has been performed by a separate formulation introduced usually during the rinse cycle of the wash.

A set of well known fabric softening agents are the tetra-alkyl quaternary ammonium halides, especially the di(hydrogenated tallow)- and distearyl-dialkyl ammonium halides. However, these are cationic softeners and are not compatible with detergents which contain an anionic component.

A further set of compounds which is believed to have a softening effect on fabrics are clays, especially the smectite type clays. Several recent publications, notably GB-A-2201172, GB-A-1400898, GB-A-1462484, GB-A-2132629 and EP 225142 describe the use of smectite type clays in various formulations.

In these, some compromise has been accepted between the cleansing and softening effectiveness of the formulations using a specific choice of

- (a) clay together with a water insoluble cationic compound and an electrically conducting metal salt (GB-A-1483627) and
- (b) a tertiary amine and clay (EP-A-0011340).

It has now been found that two of the conventional softeners, which are relatively inefficient when used individually, show an unexpectedly high softening effect when used in combination without

adversely affecting the cleansing efficiency of the formulation.

Accordingly, the present invention is a detergent powder formulation comprising one or more surfactants, a builder salt and a clay characterised in that the clay is pretreated with one or more
 5 barrier materials as hereinafter defined selected from a siloxane, a siloxane containing cationic functional groups, a polyacrylate, dialkyl citrate, alkoxyated dialkyl citrate, bis(alkyl polyoxyalkylene) citrate, alkoxyated glycerol mono- and distearates, betaines and alkoxyated N-alkyl alkanolamides prior to
 10 incorporation of the clay in the formulation.

By the expression "barrier material" as used herein and throughout the specification is meant one or more materials listed herein whenever used to pretreat a clay by coating, impregnating or otherwise having incorporated therein or on the surface thereof one
 15 or more of the materials listed whether or not such treatment results in the material acting as a protective barrier on the clay so treated.

Any of the well known surfactants can be used in the detergent compositions of the present invention. A typical list of these
 20 surfactants can be found in EP-A-225142 and in EP-A-11340.

Examples of water soluble anionic surfactants include the salts of alkyl benzene sulphonates, paraffin sulphonates, alpha-olefin sulphonates, alkyl glycol ether sulphonates, 2-acyloxy alkane-1-sulphonate and beta- alkyloxy alkane sulphonate.
 25 Similarly, salts of alkyl sulphates, alkyl polyalkoxy ether sulphates, fatty acid monoglyceride sulphates and sulphonates and alkyl phenol polyalkoxy ether sulphates may also be used.

Suitable examples of the above surfactants are linear straight chain alkyl benzene sulphonates having alkyl groups with 8-16 carbon
 30 atoms and methyl branched alkyl sulphates having 8-16 carbon atoms which are also effective.

Other anionic detergent compounds suitably for use herein include the sodium fatty acid monoglyceride sulphonates and sulphates derived from coconut oil; and sodium or potassium salts of
 35 C₈-C₁₂ alkyl phenol alkylene oxide ether sulphate containing up to

10 alkylene oxide units per molecule. Mixtures of anionic surfactants may also be used. A substantial list of such compounds can be found in e.g. McCutcheon's Dictionary of Emulsifiers and Detergents, International Edition (1981), published by the
 5 Manufacturing Confectioner Publishing Co. and in "Surfactants Europa: A Directory of Surface Active Agents available in Europe", Ed. Gordon L. Hollis, Vol 1 (1982), published by George Goodwin.

The nonionic surfactants which may be used in the present invention are condensates of an alkylene oxide e.g. ethylene oxide
 10 with a hydrophobic group to form a surfactant having an appropriate hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, suitably from 9.5 to 13.5, preferably from 10 to 12.5. The hydrophobic group may be an aliphatic or aromatic type and the length of the polyoxyethylene group condensed therewith can be
 15 readily adjusted to yield a water-soluble compound having the desired degree of HLB.

Examples of suitable nonionic surfactants include:

- (a) The polyethylene oxide condensates of alkyl phenol in which the alkyl group e.g. contains from 6 to 12 carbon atoms and in
 20 which from 3 to 30 moles, preferably 3 to 14 moles of ethylene oxide are present. Other examples include a mole of dodecylphenol condensed with 6 moles of ethylene oxide, a mole of dinonylphenol condensed with 9 moles of ethylene oxide and a mole of nonylphenol and octadecylphenol condensed with 11
 25 moles of ethylene oxide.
- (b) The nonionic surfactant may also be formed as condensation product of a mole of primary or secondary C₈-C₁₆ aliphatic alcohols with from 2 to 30 moles, preferably 2 to 9 moles of ethylene oxide.

30 Specific examples of nonionic surfactants useful for the purposes of the invention include the various grades of Dobanol (Registered Trade Mark, supplied by Shell) Lutensol (Registered Trade Mark, supplied by BASF) and Synperonics (Registered Trade Mark, supplied by ICI).

35 The amount of surfactant in the formulation is suitably from

2-30% w/w, preferably from 6-15% w/w of the total formulation.

An essential component of detergent compositions in accordance with the invention is one or more detergent builder salts which may comprise up to 70% of the composition, more typically from 5 to 70% by weight thereof. Suitable detergent builder salts useful herein can be of the polyvalent inorganic and polyvalent organic types of mixtures thereof. Examples of suitable water-soluble, inorganic alkaline detergent builder salts include the alkali metal carbonates, phosphates, pyrophosphates, tripolyphosphates and bicarbonates.

Examples of suitable organic alkaline detergency builder salts are water-soluble polycarboxylates such as the salts of nitrilotriacetic acid, lactic acid, glycollic acid and ether derivatives thereof; succinic acid, malonic acid, (ethylenedioxy)diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric acid; citric acid, aconitic acid, citraconic acid, carboxymethyloxysuccinic acid, lactoxysuccinic acid, and 2-oxy-1,1,3-propane tricarboxylic acid; oxydisuccinic acid, 1,1,2,2-ethane tetracarboxylic acid, 1,1,3,3-propane tetracarboxylic acid and 1,1,2,3-propane tetracarboxylic acid; cyclopentane-cis, cis-cis-tetracarboxylic acid, cyclopentadiene pentacarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,3,4,5-tetrahydrofuran-cis, cis, cis-tetracarboxylic acid, 2,5-tetrahydrofuran-cis-dicarboxylic acid, 1,2,3,4,5,6-hexanehexacarboxylic acid, mellitic acid, pyromellitic acid and the phthalic acid derivatives.

Water-insoluble detergent builders can also be used. A specific example of such builders are the zeolites especially the sodium type A zeolite typified by SASIL (Registered Trade Mark).

Mixtures of organic and/or inorganic builders can also be used.

Particularly preferred as builder salts are the alkali metal pyrophosphates and alkali metal tripolyphosphates.

The builder salts are suitably present in an amount from 5-70% w/w, preferably from 20-60% w/w based on the total formulation. The amount used is such that the pH of the formulation in 0.5% aqueous

solutions at 20°C is maintained suitably from 8.5-11, preferably from 9.5-10.5. In some cases it may be necessary to add buffering agents in order to control the pH value of the formulation within the desired range. Buffering agents of this type will be well known to those skilled in the art. Examples include one or more of borax, borax pentahydrate or decahydrate; glycerol and sodium carbonate.

The feature of the invention is the use of a clay component which has been pretreated with a barrier material prior to incorporation in the detergent formulation.

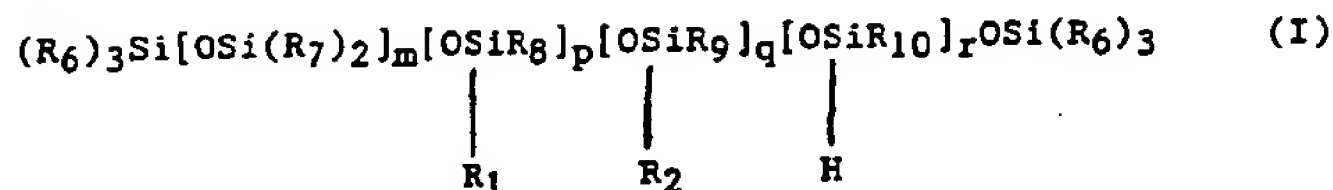
As clays may be used any aluminosilicate type material which has the ability to impart softening to fabrics laundered with a formulation containing the same. Clays having an ion-exchange capacity of at least 50 meq/100g of clay (milliequivalents per 100g of clay) are preferred. Specific examples of such clays include smectite type clays. These latter clays are multi-layered clays which layered structure is capable of increasing the volume thereof several-fold by their ability to swell or expand when in contact with water and thereby form a thixotropic gelatinious substance.

Such clays are well known in the art and are described for example in GB-A-12201172, GB-A-1400898, GB-A-1462484, GB-A-2132629 and EP-A-225142 which are incorporated herein by reference. Specific examples of clays that may be used in the present invention include bentonite, montmorillonite, nontronite, volchonskoite, saponite, hectorite, sanconite and vermiculite, and mixtures thereof.

The clays used may be hydrophilic or organophilic provided that pre-treatment thereof with the barrier materials is carried out prior to incorporation in the detergent formulation.

The barrier material used is one or more of siloxanes, siloxanes containing cationic functional groups, polyacrylates, dialkyl citrate, alkoxylated dialkyl citrate, bis-(alkylpolyoxy alkylene)citrate, alkoxylated glycerol mono- and distearates, betaines and alkoxylated N-alkyl alkanolamides.

The polysiloxanes used to treat the clays have the general formula:



wherein R_1 , R_6 , R_7 , R_8 , R_9 and R_{10} are the same or different groups of the formula $(CH_2)_tCH_3$,

$R_2 = -(CH_2)_z(OCH_2CHR_3)_x(OCH_2CHR_4)_y-OR_5$

in which each of R_3 and R_4 are H or a $-CH_3$ group such that the resultant polyoxyalkylene derivative is a polymer of ethylene oxide and/or a random or block copolymer of ethylene oxide and propylene oxide,

$R_5 = H$, a C_1-C_4 alkyl or an acetoxy group,

$x = 1-50$

$y = 0-40$

$z = 1-10$

$t = 0-21$

$m = 0-1000$

$p = 0-100$

$q = 1-50$ and

$r = 0-10$

The siloxanes (I) used as barrier materials are derivable by the reaction of a siloxane with an olefin and excess alkylene oxide. However, the product of this reaction may be used directly as the barrier material even though such a product may be a mixture of (I) and some unreacted or partially reacted materials. In such a product the siloxane (I) is a predominant component. Thus, for instance, if the reaction of all $-OSi(H)(R_{10})-$ groups in the siloxane with the alkylene oxide is complete, the value of r can be 0 in formula (I) because this will represent the absence of any unreacted $-OSi(R_{10})(H)$ groups in the siloxane used.

In compounds of the formula (I), the preferred siloxanes have the following values for the various notations used:-

m = 5-120

p = 0-40

q = 1-15

r = 0-5

5 x = 5-15

y = 1-10

z = 2-5

$R_1 = (CH_2)_tCH_3$ where t=9-19,

R_3 is H

10 $R_4 = R_6 = R_7 = R_8 = R_9 = R_{10} = -CH_3$, and

R_5 is H or $-CH_3$

The amount of clay present in the formulation is suitably from 1 to 50%, preferably 2 to 30% by weight of the total formulation.

15 The clay may be, for instance, pre-treated with the barrier material by any one of the following methods. For example it may be spray coated neat or from a suitable solvent, coated from e.g. a fluidised bed, dry-milled or a admixture of clay, barrier material and a solvent followed by evaporation of the solvent.

20 By using the treatment methods referred to above the clay may be coated, impregnated or otherwise have incorporated therein or on the surface thereof some or all of the barrier material used for the treatment. For instance, if a siloxane is used as the barrier material and the incorporation of the material onto clay is from a solution of the siloxane, the amount of polysiloxane on the clay is
25 suitably from 0.1 to 50%, preferably from 1 to 30% w/w based on the total treated clay.

The detergent formulation is a powder which can be formed by thoroughly mixing the treated clay with the other ingredients of the detergent using a high speed mixer followed, if necessary, by
30 granulation.

The detergent formulations disclosed herein can contain other materials commonly used in such compositions. For example, various soil-suspending agents such as carboxymethyl-cellulose, corrosion inhibitors, dyes, optical brighteners, suds-boosters,
35 suds-depressants, germicides, anti-tarnishing agents such as sodium

silicate, and enzymes, well known in the art for use in detergent
 5 formulations can also be employed herein. Bound water can also be
 present in said detergent formulations.

The fabrics so treated can also facilitate ironing of the
 washed fabrics.

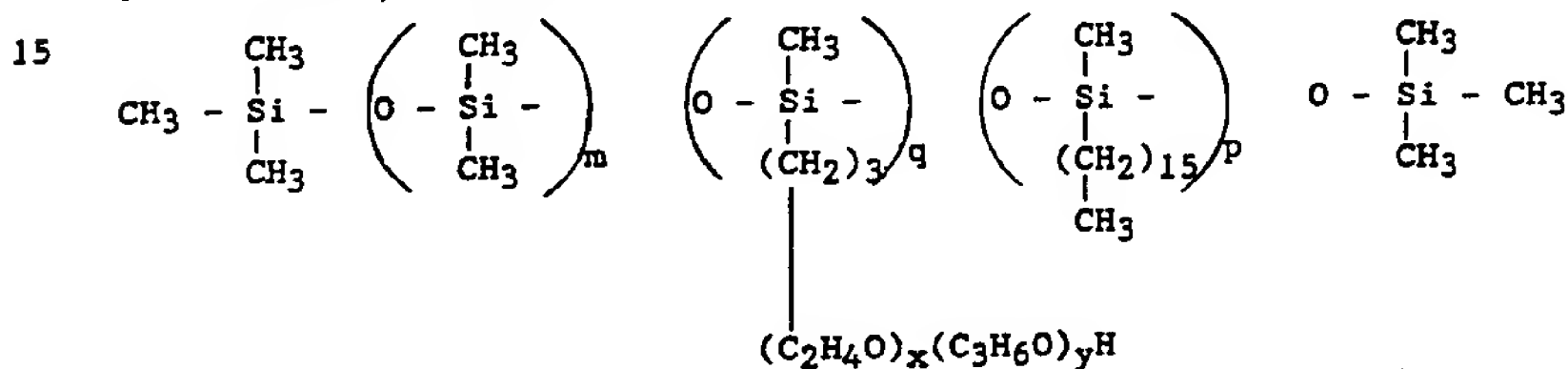
The present invention is further illustrated with reference to
 10 the following Examples and comparative tests which were all carried
 out on 400gsm Terry towelling cloth:

1. Clays

The clay tested in these Examples was Texas Bentonite clay.

2. Materials Tested

2.1 Siloxane, Product A



25 Product A, Mol.wt = 7900

$m = 40$

$q = 2.0$

$p = 10.5$

$x = 12$, and

30 $y = 4$

2.2 Bis(octadecylheptaethoxy)citrate, Product B

Product B, prepared by reacting an excess (2 moles) octadecanol
 heptaethoxy alcohol with citric acid (one mole) at elevated
 temperature (above 145°C) with stirring and continuous removal of
 35 water. The reaction mixture was then purged with nitrogen. The

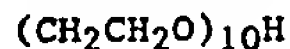
resultant product had the following ^{13}C Nmr analysis.

^{13}C NMR Analysis Results for Bis(octadecylheptaethoxy) Citrate

Esters

	Alcohol used	-(EO) ₇ OH
5	%Esterification on C ₁ and C ₃	97/86
	%Esterification on C ₂	78/74
	Remaining CH ₂ OH (%)	9/7
10	Ester per COOH	0.9/0.8
	Total Ester No.	2.7/2.5

2.3 N-octadecyloctadecanoamide 10 mole ethoxylate, Product C



15	COC ₁₇ H ₃₅
----	-----------------------------------

N-Octadecyl octadecanoamide was prepared by heating octadecyl isocyanate with an equimolar amount of stearic acid in refluxing xylene at 150°C for 4.5h according to the procedure of Agre, Dinga and Pflaum, J. Org. Chem., 1955, 20, 695.

20 The amide was converted into the corresponding ethoxylated derivative by reaction of the amide in an autoclave with 10 moles of ethylene oxide at a temperature of 170-180°C and a pressure of 35-40 psig according to standard procedures. (See for example, Malkemus, J. Amer. Oil Chemists' Soc., 1956, 33, 571). Potassium hydroxide
25 (0.2%) was used as catalyst.

2.4 Glycerol monostearate 3 mole ethoxylate, Product D

Glycerol esters of stearic acid was synthesised by heating one mole of stearic acid with 1 mole of glycerol at 180-240°C until the calculated quantity of water distils.

30 The ethoxylated glycerol stearate was then prepared by reaction of the glycerol mono stearate in an autoclave with the 3 moles of ethylene oxide at a temperature of 140°C and a pressure of 4.5 bar according to standard procedures. (See for example, Malkemus, J. Amer. Oil Chemists' Soc., 1956, 33, 571). Potassium hydroxide
35 (0.15%) was used as the catalyst.

3. Performance Testing

3.1 Each Barrier Material Alone (Comparative Tests not according to the invention).

3.1.1 On Cloth Surface

5 To assess whether the barrier material would confer softening when present on the cloth surface, the siloxane was deposited onto cloth as a 1% solution in chloroform. After drying at room temperature for several hours, the treated cloths (400gsm Terry towelling) were assessed for softness by a small test panel against
10 cloths treated by the solvent only, and ranked. Products A, B, C and D all gave good softening.

3.1.2 Presence of Barrier Material in Wash Liquor

 To simulate washing machine conditions, cloths were treated in a beaker at typical commercial detergent concentrations (New system
15 Persil Automatic, Registered Trade Mark ex Lever Bros) (hereafter NSPA) of 10g/L at 60°C. After drying and conditioning for 24 hours at 20°C and 60% relative humidity, the cloths were ranked for softness by panel assessment and compared with cloths treated by NSPA alone and Bold 3 (a powdered detergent/softener ex Procter and
20 Gamble).

 Results showed that NSPA plus 1% of any of Product A, B, C, or D gave no detectable improvement in softness compared with NSPA alone but all were significantly inferior to Bold 3.

3.2 Clay Alone (Comparative Test not according to the invention).

25 Results from screening test showed that Terry towelling treated with NSPA plus 10% levels of Texas bentonite clay alone gave better softening than by treatment with NSPA alone as judged by a test panel. However, softening did not approach that obtained by washing in Bold 3. Numbers in the Table below correspond to softness
30 ranking of treatment i.e. 1 means softest cloth, 3 means hardest assessed.

	<u>Panellist</u>	<u>NSPA</u>	<u>NSPA + 10%</u>	
			<u>Texas Bentonite</u>	<u>Bold 3</u>
	A	3	2	1
	B	3	2	1
5	C	3	2	1
	D	3	2	1
	Total Rank	12	8	4

Conclusion

10 It appeared that although the barrier materials conferred softening when they reached and adhered to the cloth surface, they could not do so in the presence of a typical commercial detergent powder (NSPA). Untreated clay gives some softening but not of the order of Bold 3.

15 3.3 Clays Coated with Barrier Materials A,B,C,D. (Present Invention)

Clay provided a delivery system to enable the softening properties of the additives to be transferred to the fabric surface.

3.3.1 Coating of Barrier Materials A,B,C,D onto Clay

20 For the initial method of coating, at 10% by weight of clay, 20g barrier material was dissolved (or dispersed) in approximately 200cm³ chloroform and 180g Texas bentonite clay was added. The solvent was evaporated, followed by oven drying of the clay for 2 hours at 70°C. Any lumps of clay were ground to a fine powder.

3.3.2 Softness

25 Softness Screening in Wash Liquor

In this screening test method, 10% by weight of the coated clay was added to the NSPA prior to the test wash. The results from these trials show that NSPA plus 10% Texas bentonite, coated with 10% additive A, B, C, or D, gives softness approaching or exceeding 30 that of Bold 3 and therefore exceeding that of uncoated Texas bentonite. (Numbers correspond to total rank of cloth from 4 panellists).

i) Siloxane, Product A

	<u>NSPA</u>	<u>NSPA +10% Coated clay</u>	<u>NSPA+10% Coated clay</u>	<u>Bold 3</u>
35	16	11	8	5

ii) DiOctadecylcitrate 14 mole ethoxylate, Product B

<u>NSPA</u>	<u>NSPA+5%</u>	<u>NSPA+10%</u>	<u>Bold 3</u>
	<u>coated clay</u>	<u>coated clay</u>	
14	11	8	7

5

iii)

<u>NSPA</u>	<u>NSPA+10% clay</u>	<u>NSPA+10% clay</u>	<u>Bold 3</u>
	<u>coated with</u>	<u>coated with</u>	
	<u>octadecyl-</u>	<u>glycerol</u>	
	<u>octadecanoamide</u>	<u>monostearate</u>	
	<u>10 mole ethoxylate,</u>	<u>3 mole ethoxylate,</u>	
	<u>Product E</u>	<u>Product D</u>	

10

15	8	7	10
----	---	---	----

15

20

25

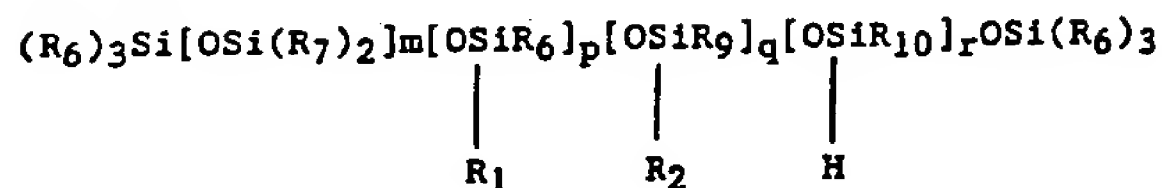
30

35

Claims:

1. A detergent powder formulation comprising one or more surfactants, a builder salt and a clay characterised in that the clay is pretreated with one or more of the barrier materials selected from a siloxane, a siloxane containing functional groups, a polyacrylate, dialkyl citrate, alkoxyated dialkyl citrate, bis(alkyl polyoxyalkylene) citrate alkoxyated glycerol mono- and di-stearates, betaines and alkoxyated N-alkyl alkanolamides prior to incorporation of the clay in the formulation.
2. A formulation according to Claim 1 wherein the clay is pretreated with the barrier material by coating, impregnating or otherwise having incorporated therein or on the surface thereof one or more of the barrier materials.
3. A formulation according to Claim 1 or 2 wherein the clay is an aluminosilicate having an ion-exchange capacity of at least 50 meg/100g of clay.
4. A formulation according to Claim 3 wherein the clay is a smectite type clay.
5. A formulation according to any one of the preceding Claims wherein the clay is selected from bentonite, montmorillonite, nontronite, volchonskite, saponite, hectorite, sanconite, vermiculite and mixtures thereof.
6. A formulation according to any one of the preceding Claims wherein the clay is present in the formulation in an amount from 1 to 50%w/w.
7. A formulation according to any one of the preceding Claims

wherein the barrier material is a polysiloxane of the general formula.



5

wherein R₁, R₆, R₇, R₈, R₉ and R₁₀ are the same or different groups of the formula (CH₂)_tCH₃,

r₂ = -CH₂)_z(OCH₂.CHR₃)_x(OCH₂CHR₄)_y-OR₅

10

in which each of R₃ and R₄ are H or a -CH₃ group such that the resultant polyoxalkylene derivative is a polymer of ethylene oxide and propylene oxide,

R₅ = H, a C₁-C₄ alkyl or an acetoxy group,

15

x = 1-50

y = 0-40

z = 1-10

t = 0-21

m = 0-1000

20

p = 0-100

q = 1-50 and

r = 0-10.,

8. A formulation according to any one of the preceding Claims wherein the clay has from 0.1-50%w/w of the barrier material based on the total treated clay.

25

9. A formulation according to any one of the preceding Claims wherein the formulation is prepared by thoroughly mixing the treated clay with the other ingredients of the formulation using a high speed mixer followed optionally by granulation.

30

35

THIS PAGE BLANK (USPTO)